Designation: E1447 – 09 (Reapproved 2016)

Standard Test Method for Determination of Hydrogen in Titanium and Titanium Alloys by Inert Gas Fusion Thermal Conductivity/Infrared Detection Method[1]

This standard is issued under the fixed designation E1447; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method applies to the determination of hydrogen in titanium and titanium alloys in concentrations from 0.0006 % to 0.0260 %.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazards, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C696 Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets
E50 Practices for Apparatus, Reagents, and Safety Considerations for Chemical Analysis of Metals, Ores, and Related Materials
E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials
E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method
E1914 Practice for Use of Terms Relating to the Development and Evaluation of Methods for Chemical Analysis (Withdrawn 2016)[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, see Terminology E135 and E1914.

4. Summary of Test Method

4.1 The specimen, contained in a small, single-use graphite crucible, is fused under a flowing carrier gas atmosphere. Hydrogen present in the sample is released as molecular hydrogen into the flowing gas stream. The hydrogen is separated from other liberated gases such as carbon monoxide and finally measured in a thermal conductivity cell.

4.2 Alternatively, hydrogen is converted to water by passing the gas stream over heated copper oxide and subsequently measuring in an appropriate infrared (IR) cell.

4.3 This test method is written for use with commercial analyzers equipped to perform the above operations automatically and is calibrated using reference materials of known hydrogen content.

5. Significance and Use

5.1 This test method is intended to test for compliance with compositional specifications. It is assumed that all who use this test method will be trained analysts capable of performing common laboratory procedures skillfully and safely. It is expected that the work will be performed in a properly equipped laboratory.

6. Interferences

6.1 The elements ordinarily present in titanium and its alloys do not interfere.

7. Apparatus

7.1 *Fusion and Measurement Apparatus*—Automatic hydrogen determinator, consisting of an electrode furnace or induction furnace; analytical gas stream impurity removal systems; auxiliary purification systems and either a thermal conductivity cell hydrogen measurement system or an infrared hydrogen measurement system (Note 1).

NOTE 1—The apparatus and analysis system have been previously described in the Apparatus and Apparatus and Equipment sections of Test

---

[1] This test method is under the jurisdiction of ASTM Committee E01 on Analytical Chemistry for Metals, Ores, and Related Materials and is the direct responsibility of Subcommittee E01.06 on Ti, Zr, W, Mo, Ta, Nb, Hf, Re.

Current edition approved Aug. 1, 2016. Published August 2016. Originally approved in 1992. Last previous edition approved in 2009 as E1447 – 09. DOI: 10.1520/E1447-09R16.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

Methods C696. Several models of commercial analyzers are available and presently in use in industry. Each has its own unique design characteristics and operational requirements. Consult the instrument manufacturer's instructions for operational details.

7.2 *Graphite Crucibles*—The crucibles are machined from high-purity graphite. Use the size crucibles recommended by the manufacturer of the instrument.

7.3 *Crucible Tongs*—Capable of handling recommended crucibles.

7.4 *Tweezers or Forceps*—For contamination-free sample handling.

8. Reagents and Materials

8.1 *Acetone,* low-residue reagent grade or higher purity.

8.2 *Sodium Hydroxide on Clay Base,* commonly known as Ascarite II.

8.3 *High-Purity Carrier Gas (99.99 %)*—Argon, nitrogen, or helium (Note 2).

NOTE 2—Carrier gases vary by instrument model and include high-purity argon, nitrogen, and helium. Consult instrument manufacturer's instructions for proper gas recommendation.

8.4 *High-Purity Tin Metal (Low Hydrogen)*—Use the purity specified by the instrument manufacturer.

8.5 *Magnesium Perchlorate, Anhydrone.*

8.6 *Molecular Sieve*—Characteristics specified by the instrument manufacturer.

8.7 *Schutze Reagent*—Iodine pentoxide over silica gel.

8.8 *Copper Oxide Wire*—To convert hydrogen to water in IR-detection instruments. Characteristics specified by the instrument manufacturer.

9. Hazards

9.1 For hazards to be observed in the use of this test method, refer to Practices E50.

9.2 Use care when handling hot crucibles and operating electrical equipment to avoid personal injury by either burn or electrical shock.

10. Preparation of Apparatus

10.1 Assemble the apparatus as recommended by the manufacturer.

10.2 Test the furnace and analyzer to ensure the absence of gas leaks and make the required electrical power and water connections. Prepare the apparatus for operation in accordance with the manufacturer's instructions. Make a minimum of two determinations using a specimen as directed in 13.2 before attempting to calibrate the system or to determine the blank.

11. Sample Preparation

11.1 Use solid form specimens prepared as directed in 11.2. Specimens must be of an appropriate size to fit into the graphite crucible and should not exceed 0.30 g in weight.

11.2 Cut the specimen to the approximate size of 0.15 g to 0.30 g (preferably by shearing). For specimens of unknown history or suspected surface contamination, abrade specimen surfaces with a clean file to remove contamination. Other methods, such as turning down on a lathe, may be employed for reducing sample size and removing the surface of the sample (Note 3). Rinse the sample in acetone, and air dry. Weigh to ± 0.001 g. Samples shall be handled only with tweezers or forceps after cleaning and weighing to prevent contamination.

NOTE 3—Regardless of the method used, the sample must not be allowed to overheat, as this will adversely affect the results of the analysis. Indications that the sample has overheated while being worked may include discoloration of the metal or the sample becoming too hot to handle without tools.

12. Calibration

12.1 *Calibration Reference Materials*—Select only titanium or titanium alloy reference materials (Note 4).

NOTE 4—Gas dosing: it is satisfactory to calibrate the unit by dosing known volume(s) of hydrogen gas into the detection system. If the instrument has this feature, refer to the manufacturer's recommended procedure. In this case instrument response must always be verified by analyzing titanium or titanium alloy reference materials.

12.2 *Determination of Crucible/Tin Blank Reading:*

12.2.1 If the instrument is equipped with an electronic blank compensator, adjust to zero, and proceed with the determination of the blank value.

12.2.2 Make at least three blank determinations as directed in 13.2 using the weight of tin flux as recommended by the instrument manufacturer (Note 5). Use a fresh crucible each time.

NOTE 5—Flux weight is dependent upon the model of the instrument and the manufacturer's instruction. Refer to the manufacturer's instructions and recommendations.

12.2.3 If the average blank value exceeds 0.0000 % ± 0.0001 %, or a standard deviation for the three consecutive values exceeds ± 0.0001 %, then determine the cause, make necessary corrections, and repeat 12.2.1 and 12.2.2 (Note 6).

NOTE 6—Refer to the instrument manufacturer's instructions concerning the troubleshooting and correction of blank determinations not meeting the above criterion.

12.2.4 Enter the average blank value in the appropriate mechanism of the analyzer (Note 7) according to the manufacturer's instruction. This mechanism will electronically compensate for the blank value.

NOTE 7—If the unit does not have this function, the average blank must be subtracted from the total result.

12.3 *Calibration Procedure:*

12.3.1 Prepare at least four 0.15 g to 0.30 g specimens (at least one specimen if calibrating by gas dosing) of a titanium hydrogen reference material as directed in 11.2. This titanium hydrogen reference material should have a hydrogen content greater than or approximately equal to the unknown samples within the scope of this test method (0.0006 % to 0.0260 %).

12.3.2 Follow the calibration procedure recommended by the manufacturer. Analyze at least three reference material specimens to determine the calibration slope (Note 8). Treat each specimen as directed in 13.2 before proceeding to the next one (Note 9).

NOTE 8—For calibration by gas dosing, perform at least three gas dose analyses to determine the calibration slope. Refer to instrument manufacturer's instructions.

NOTE 9—Some instruments have expanded computer capabilities that allow multi-point calibration which may improve the accuracy and precision of the calibration over the single-point calibration methodology as tested in the current interlaboratory study (ILS).

12.3.3 Confirm the calibration by analyzing a specimen of titanium hydrogen reference material (Note 10). The ILS used an acceptance criterion where the value fell within the allowable limits of the certified value. An alternate procedure can be implemented where this value should agree with the certified value within the limits of a prediction interval calculated using Eq 1. The prediction interval is defined as the range of values bounded by the analysis value $-p$ and the analysis value $+p$. If the prediction interval does not encompass the certified value, determine and correct the cause, and repeat 12.3.1 and 12.3.2 (Note 11). Either acceptance limit criterion is acceptable for routine operation.

NOTE 10—Confirmation of the calibration does not ensure accuracy. The accuracy of this test method is largely dependent upon the absence of bias in the hydrogen values assigned to the reference materials and upon the homogeneity of these materials.

NOTE 11—See the instrument manufacturer's instructions concerning the troubleshooting and correcting of errant calibration.

$$p = t \cdot \left(1 + \frac{1}{\sqrt{n}} \right) \cdot s \tag{1}$$

where:

p = one-half the prediction interval,
n = number of replicates used in 12.3.2,
t = student's t chosen for the 95 % confidence level for n replicate measurements (for example: $t = 2.35$ when $n = 3$, 2.13 when $n = 4$, 2.02, when $n = 5$), and
s = standard deviation of n replicates in 12.3.2 (Note 12).

NOTE 12—Here, s should be comparable to S_m, the repeatability standard deviation, given in Table 1. If s » S_m, there is evidence that the repeatability of the particular instrument is not acceptable for use with this test method. The user should determine and correct the cause, and repeat 12.3.1 through 12.3.3.

12.3.4 Confirm calibration linearity by analyzing a mid-range (Note 13) titanium hydrogen reference material, using the limits stated on the certified value as an acceptance range. Alternatively, analyze at least three specimens of a mid-range (Note 13) titanium hydrogen reference material. Calculate the average and standard deviation(s) of these results. In the absence of bias among the reference materials, the average result for this reference material should agree with the certified value within a prediction interval defined by the repeatability of the measurement system at the mid-range of the calibration (Note 14). This prediction interval may be calculated using Eq 1 and the s and n values for the mid-range reference material. If the prediction interval does not encompass the certified value, determine and correct the cause and repeat 12.3.1 and 12.3.4 (Note 15).

NOTE 13—Commercially available reference materials are not always available at the concentration required to have a true mid-point check. The mid-range material must have a hydrogen concentration that is above the limit of detection, but below that of the high calibration point, preferably as close to the mid-point of the calibration curve as possible.

NOTE 14—Typically, repeatability standard deviation is a function of the concentration of the analyte. Compare the values labeled *ILS Analyzed Mean* in Table 1 with the values for *Minimum SD* (S_m) to see a typical trend for laboratories using this test method. If your results are not comparable, investigate and correct the cause.

NOTE 15—The presence of bias between the reference material used in 12.3.2 and the reference material used in 12.3.4 may cause the calibration to appear to be non-linear. This cannot be corrected by making adjustments to the instrument.

12.3.5 One or more continuing calibration verifications must be performed prior to and upon completion of a period of continuous operation, and throughout this period with a predetermined minimum frequency to be established by each individual test facility. The acceptance range for the verification material may be the limits stated on the certified value for the reference material, or may be calculated using Eq 1 and the s and n values for multiple analyses of the verification material. If a continuing calibration verification indicates an out of calibration condition, stop analysis. Results must be supported by acceptable preceding and subsequent verifications to be reported.

12.4 *Calibration Frequency:*

12.4.1 It is the responsibility of the user to document the frequency of blank determination (12.2.1 – 12.2.4), routine calibration and confirmation (12.3.2 and 12.3.3) and linearity confirmation (12.3.4), and the conditions under which blank determination or recalibration, or both, beyond this frequency

TABLE 1 Hydrogen in Titanium Metal Statistical Information[A]

Material	# Labs	Certified Value (µg/g)	ILS Analyzed Mean (µg/g)	Difference (µg/g)	Certified Precision (µg/g)	Minimum SD (S_m, Practice E1601)	Reproducibility SD (S_R, Practice E1601)	Reproducibility Index (R, Practice E1601)	$R_{rel\ \%}$
BCR 318[B]	10	12.2	11.4	0.8	0.8	0.44	1.01	2.83	24.9
CEZUS LH[C]	11	...	20.3	...	...	1.64	2.63	7.36	36.3
NBS 352[D]	11	32	27.4	4.6	2	1.43	1.96	5.47	20.0
CEZUS TIV25[C]	11	...	90.2	...	...	1.44	5.31	14.90	16.5
NBS 353[D]	11	98	95.8	2.2	5	3.42	4.00	11.19	11.7
NBS 354[D]	11	215	213.2	1.8	6	3.36	3.66	10.24	4.80
NIST 2454[E]	11	...	219.5	...	...	5.80	11.35	31.78	14.5
CEZUS HH[C]	10	...	260.1	...	...	4.45	11.72	32.80	12.6

[A] ILS conducted in accordance with Practice E1601, Plan A.
[B] Certified Reference Material: Commission of the European Communities, Community Bureau of Reference.
[C] Reference Material: CEZUS, Ugine, France.
[D] Standard Reference Material: National Institute of Standards and Technology, formerly National Bureau of Standards.
[E] Standard Reference Material (under development): National Institute of Standards and Technology. Material is in chip form.

is required (examples may include changing reagents, changing gas cylinders or a personnel shift change).

13. Procedure

13.1 Assemble the apparatus and condition it as directed in Section 10.

13.2 *Procedure for Operation:*

13.2.1 Set the analyzer to operate mode.

13.2.2 Prepare a 0.15-g to 0.30-g specimen as directed in 11.2.

13.2.3 Place a 0.15-g to 0.30-g specimen in the loading device. If the instrument does not have this feature, refer to the manufacturer's recommended procedure regarding entry of sample.

13.2.4 Enter the sample weight as recommended by the manufacturer.

13.2.5 Place a crucible containing high-purity tin as measured in 12.2.2 on the furnace electrode/pedestal assembly and close the furnace.

13.2.6 Start the analysis cycle according to the manufacturer's recommended procedure.

14. Calculation

14.1 The reading will be direct if the blank and weight have been entered correctly into the appropriate portion of the analyzer (Note 16).

NOTE 16—If the analyzer does not offer these functions, calculate the hydrogen content by the following method: Dial the sample weight or a multiple of the sample weight on the weight compensator and use the following formula (Eq 2) for the calculation of the result:

$$\text{Hydrogen, \%} = \frac{(A - B) \times C}{D} \quad (2)$$

where:

A = sample digital volt meter (DVM) reading,
B = blank DVM reading,
C = weight compensator setting, and
D = sample weight, g.

15. Precision and Bias

15.1 *Precision*[4]—Eleven laboratories cooperated in testing eight samples in triplicate. The data are presented in Table 1. The testing and statistical analysis were performed in accordance with the provisions of Practice E1601, Plan A. Six instruments were of the thermal conductivity hydrogen measurement system configuration and five instruments were of the infrared hydrogen measurement system configuration. Calibration was performed utilizing a single calibration material (NBS 354, 215 µg/g ± 6 µg/g).

15.2 *Bias*—Information on the accuracy of this test method is incomplete at this time. The accuracy of this test method may be judged by comparing the results obtained from certified reference materials with their certified values for hydrogen.

16. Keywords

16.1 hydrogen; inert gas fusion; titanium; titanium alloys

---

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:E01-1004.